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LOW SELECTIVITY DEPOSITION METHODS

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INVENTOR

Garry A. Mercaldi

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# LOW SELECTIVITY DEPOSITION METHODS

## TECHNICAL FIELD

This invention relates to methods of atomic layer deposition and methods of low selectivity chemical vapor deposition.

## BACKGROUND OF THE INVENTION

Atomic layer deposition (ALD) is recognized as a deposition technique that forms high quality materials with minimal defects and tight statistical process control. Even so, it is equally recognized that ALD can have limited application. In some circumstances, the theoretically expected quality of an ALD layer is not achieved.

It can be seen that a need exists for an ALD method that forms a layer without introducing intolerable defects into the material.

## BRIEF DESCRIPTION OF THE DRAWINGS

Preferred embodiments of the invention are described below with reference to the following accompanying drawings.

Fig. 1 shows a cross-sectional fragmentary view of a deposition substrate at one processing step in accordance with an aspect of the invention.

Fig. 2 shows the deposition substrate of Fig. 1 at a processing step subsequent to that shown in Fig. 1.

Fig. 3 shows the deposition substrate of Fig. 1 at an alternative processing step subsequent to that shown in Fig. 1.

Fig. 4 shows the deposition substrate of Fig. 1 at a processing step subsequent to that shown in Fig. 3.

Fig. 5 shows a cross-sectional fragmentary view of a semiconductive wafer portion at a processing step in accordance with an aspect of the invention.

Fig. 6 shows the semiconductive wafer of Fig. 5 at a processing step subsequent to that shown in Fig. 5.

#### SUMMARY OF THE INVENTION

One aspect of the invention provides a deposition method that includes forming a nucleation layer over a substrate, forming a layer of a first substance at least one monolayer thick chemisorbed on the nucleation layer, and forming a layer of a second substance at least one monolayer thick chemisorbed on the first substance. A chemisorption product of the first and second substance may include silicon and nitrogen, or aluminum and oxygen, or tantalum and oxygen. Also, the nucleation layer may comprise silicon nitride, aluminum oxide, or tantalum oxide. A thickness of the nucleation layer may be less than about 20 Angstroms.

In another aspect of the invention, a low selectivity deposition method includes forming a first part of a nucleation layer on a first

surface of a substrate and forming a second part of a nucleation layer on a second surface of a substrate. A deposition layer may then be formed on the first and second parts of the nucleation layer substantially non-selectively on the first part of the nucleation layer compared to the second part. Substantially non-selective deposition occurs even though the first and second surfaces of the substrate exhibit a property of the deposition layer forming less readily on the first surface compared to the second surface. The deposition layer may comprise a monolayer of a first chemisorbed specie. The deposition layer may be formed by chemical vapor deposition or atomic layer deposition. The first and second part of the nucleation layer may be formed simultaneously. Also, the nucleation layer may form substantially non-selectively on the first surface of the substrate compared to the second surface. Further, a thickness of the first part of the nucleation layer may be greater than 50% of a thickness of the second part, or even greater than 80% of the thickness of the second part. The first surface of the substrate may exhibit a property of chemisorbing the first specie at a slower rate compared to the second surface.

In another aspect, a deposition method includes simultaneously forming a first part of a nucleation layer on an insulative oxide material and a second part of the nucleation layer on a semiconductive material. The nucleation layer may be contacted with an initiation precursor. An initiation layer at last one monolayer thick may be formed on the first

and second parts of the nucleation layer substantially non-selectively on the first part of the nucleation layer compared to the second part.

In another deposition method, a nucleation layer comprising silicon and nitrogen may be formed substantially non-selectively on a first and a second surface of a substrate. A monolayer of a first substance may be chemisorbed on the nucleation layer. A monolayer of a second substance may be chemisorbed on the first substance, wherein a chemisorption product of the first and second substances comprises silicon nitride.

In a still further aspect, a deposition method may include atomic layer depositing a nucleation substance chemisorbed on a first surface and a second surface of a substrate substantially non-selectively. The first surface may exhibit a property of chemisorbing an atomic layer deposition precursor at a slower rate compared to the second surface. Also, the nucleation substance may exhibit a property of chemisorbing the precursor at an approximately equal rate over the first surface compared to over the second surface.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

This disclosure of the invention is submitted in furtherance of the constitutional purposes of the U.S. Patent Laws "to promote the progress of science and useful arts" (Article 1, Section 8).

Atomic layer deposition (ALD) involves formation of successive atomic layers on a substrate. Such layers may comprise an epitaxial, polycrystalline, amorphous, etc. material. ALD may also be referred to as atomic layer epitaxy, atomic layer processing, etc. Further, the invention may encompass other deposition methods not traditionally referred to as ALD, for example, chemical vapor deposition (CVD), but nevertheless including the method steps described herein. The deposition methods herein may be described in the context of formation on a semiconductor wafer. However, the invention encompasses deposition on a variety of substrates besides semiconductor substrates.

In the context of this document, the term "semiconductor substrate" or "semiconductive substrate" is defined to mean any construction comprising semiconductive material, including, but not limited to, bulk semiconductive materials such as a semiconductive wafer (either alone or in assemblies comprising other materials thereon), and semiconductive material layers (either alone or in assemblies comprising other materials). The term "substrate" refers to any supporting structure, including, but not limited to, the semiconductive substrates described above.

Described in summary, ALD includes exposing an initial substrate to a first chemical specie to accomplish chemisorption of the specie onto the substrate. Theoretically, the chemisorption forms a monolayer that is uniformly one atom or molecule thick on the entire exposed initial







create thickness variations in the deposited material. Also, for example, a desire may exist to simultaneously deposit a material over two dissimilar types of substrate. A surface of borophosphosilicate glass (BPSG) and a surface of polysilicon can be two dissimilar types of substrate. Observations indicate that formation of silicon nitride by ALD simultaneously on BPSG and polysilicon produces a thickness variation in the deposited silicon nitride. The thickness of the silicon nitride deposited on the BPSG can be less than 50% of the thickness of the silicon nitride deposited on the polysilicon. A variety of other circumstances are conceivable wherein a substantially uniform thickness of a material deposited by ALD is desired on dissimilar portions of a substrate, such as a semiconductive substrate compared to an insulative or a conductive substrate.

According to one aspect of the invention, a deposition method may include forming a nucleation layer over a substrate. The nucleation layer may exhibit a first value of an electrical property, for example, dielectric constant, conductivity, current leakage, permittivity, capacitance, etc. Turning to Fig. 1, a substrate 2 is shown including a first part 4 and a second part 6. Second part 6 may comprise a composition different from first part 4 or second part 6 may comprise the same composition but exhibit a property that causes deposition to occur more readily on second part 6 compared to first part 4. Fig. 2 shows a deposition layer 8 formed on first part 4 and second part 6 of substrate 2. Notably, the

1 thickness of deposition layer 8 that is over first part 4 is less than 50%  
2 of a thickness of deposition layer 8 that is over second part 6.

3 There can be at least one advantage of providing a nucleation  
4 layer over a substrate prior to performing some types of deposition, for  
5 example ALD. The nucleation layer may operate to provide at least  
6 somewhat uniform surface properties for the deposition and decrease  
7 thickness variations such as shown in Fig. 2. Even so, a nucleation layer  
8 may interface between a substrate and a subsequently deposited  
9 deposition layer in a manner that only insignificantly influences the  
10 overall properties of the combined nucleation and deposition layer. That  
11 is, a deposition layer deposited directly on a substrate without a  
12 nucleation layer generally will possess some designated purpose or  
13 designated property. A nucleation layer may be selected such that only  
14 an insignificant impact is imposed upon the desired purpose or property.  
15 Accordingly, a nucleation layer may find advantageous use even in  
16 circumstances where a substrate possesses both a homogeneous  
17 composition and homogeneous surface properties. Such a nucleation  
18 layer may interface between a substrate and a deposition layer to  
19 enhance the rate of formation of the deposition layer or to otherwise  
20 provide an advantageous property or result. For example, a first  
21 monolayer of a first chemisorbed specie may form more rapidly over  
22 BPSG if a nucleation layer is first formed.

1 In addition to composition and surface properties, the thickness of  
2 a nucleation layer may also influence its suitability. At times, ALD is  
3 selected with the desire to form high quality very thin layers of material.  
4 A nucleation layer may be selected that only insignificantly impacts the  
5 deposition layer. However, as the thickness of a nucleation layer  
6 increases and approaches or exceeds the thickness of a deposition layer,  
7 the potential advantages of selecting ALD for forming a layer of the  
8 material may be diminished. At the optimum, a nucleation layer having  
9 a thickness of only one atom or molecule may be formed to minimize  
10 any potential impact. However, a more thick nucleation layer may also  
11 provide little impact. Accordingly, a thickness of a nucleation layer may  
12 comprise less than about 20 Angstroms. Further, the thickness may  
13 comprise less than about 6 Angstroms. Still further, the thickness may  
14 comprise about 2.5 Angstroms. A monolayer of silicon nitride may  
15 comprise about 2.5 Angstroms.

16 In Fig. 3, a nucleation layer 10 is shown formed over substrate 2.  
17 In the illustration provided, substrate 2 includes first part 4 on which  
18 deposition occurs less readily compared to second part 6. As indicated,  
19 such a property may be caused by first part 4 possessing a different  
20 composition than second part 6 or exhibiting a different surface property  
21 than second part 6. Such is in contrast to another advantageous use of  
22 nucleation layer 10 even when a substrate possesses homogeneous  
23 composition and exhibits homogeneous surface properties.

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As shown in Fig. 4, a deposition layer 12 may be formed on nucleation layer 10 without the thickness variation illustrated in Fig. 2. Deposition layer 12 may be formed by any deposition method presently known to those skilled in the art or later developed, but preferably by ALD as defined herein. Other deposition methods may also be suitable. In the present aspect of the invention, a suitable deposition method may include forming a layer of a first substance at least one monolayer thick chemisorbed on the nucleation layer and forming a layer of a second substance at least one monolayer thick chemisorbed on the first substance. A chemisorption product of the layers may comprise deposition layer 12. Deposition layer 12 may exhibit a second value of the electrical property exhibited by nucleation layer 10 at a first value. Examples of electrical properties are listed above. Deposition layer 12 and nucleation layer 10 combined may exhibit a third value of the electrical property that is more near the second value than the first value. The third value and second value may be approximately equal. The method may include at least once additionally forming successive monolayers of the first substance and the second substance. In such case, all monolayers may be comprised by deposition layer 12.

Nucleation layer 10 may possess a variety of compositions and exhibit a variety of properties and still comprise a suitable interface between deposition layer 12 and a substrate, for example substrate 2. For example, nucleation layer 10 may comprise a compound the same as

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1 a deposition product of the first and second substances in the  
2 chemisorbed monolayers described above. For example, a chemisorption  
3 product of the first and second substance may comprise silicon and  
4 nitrogen. A nucleation layer may also comprise silicon and nitrogen.  
5 More specifically, the chemisorption product that produces deposition  
6 layer 12 may comprise silicon nitride and nucleation 10 may also  
7 comprise silicon nitride.

8 A nucleation layer may comprise an approximately homogeneous  
9 composition. In an approximately homogeneous composition, only  
10 insignificant differences in composition exist throughout the nucleation  
11 layer. However, a nucleation layer may also possess a composition  
12 wherein one part of the nucleation layer differs from a composition of  
13 another part of the nucleation layer as to a component, a proportion of  
14 a component, or both. One example is a nucleation layer that comprises  
15 silicon nitride but a part of the nucleation layer further comprises  
16 oxygen, for example, comprising silicon oxynitride.

17 In another aspect of the invention, a deposition method includes  
18 forming a first part of a nucleation layer on a first surface of a  
19 substrate and forming a second part of a nucleation layer on a second  
20 surface of the substrate. Forming the first and second part of the  
21 nucleation layer may occur simultaneously. Alternatively, the first part  
22 and the second part of the nucleation layer may be formed separately.  
23 When formed simultaneously, the nucleation layer may form substantially

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non-selectively on the first surface of the substrate compared to the second surface. The thickness of a nucleation layer is one measure of the selectivity of forming a nucleation layer. That is, non-selective formation of a nucleation layer may occur when the thickness of the first part of the nucleation layer on the first surface of a substrate is greater than 50% of the thickness of the second part formed on the second surface of the substrate. More particularly, non-selective formation occurs when the thickness of the first part is greater than 80% of the thickness of the second part.

One advantage of the present invention is that substantially non-selective formation of a nucleation layer may occur even though ALD on the same surface occurs selectively, that is, at a greater than 2 to 1 ratio of deposition rate. Such a deposition may produce a deposition layer having a thickness over the first surface that is less than 50% of the thickness over the second surface.

A variety of nucleation layer compositions are conceivable just as a variety of nucleation layer thicknesses and selectivities are conceivable. The second part of the nucleation layer on the second surface of the substrate may comprise a plurality of components also comprised by the first part. For example, the first and second parts of the nucleation layer may comprise silicon nitride. Further, the first and second parts of the nucleation layer may even consist essentially of the same components in approximately same proportions. For example, the first







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1 monolayer of a first chemisorbed precursor may then be formed on the  
2 nucleation layer also by ALD.

3 Often, traditional ALD occurs within an often-used range of  
4 temperature and pressure and according to established purging criteria  
5 to achieve the desired formation of an overall ALD layer one monolayer  
6 at a time. Even so, ALD conditions can vary greatly depending on the  
7 particular precursors, layer composition, deposition equipment, and other  
8 factors according to criteria known by those skilled in the art.  
9 Maintaining the traditional conditions of temperature, pressure, and  
10 purging minimizes unwanted reactions that may impact monolayer  
11 formation and quality of the resulting overall ALD layer. Accordingly,  
12 operating outside the traditional temperature and pressure ranges may  
13 risk formation of defective monolayers.

14 In accordance with the present aspect of the invention, observations  
15 indicate that increasing temperature or pressure or both can produce the  
16 effect of reducing the selectivity of an otherwise selective monolayer  
17 formation step. In the various aspects of the invention, temperature may  
18 remain below about 550 Celsius ( $^{\circ}\text{C}$ ) and pressure may remain below  
19 about 20 Torr. The increased temperature, pressure, or both  
20 correspondingly increases the likelihood that a deposition specie will  
21 chemisorb substantially non-selectively on the first and second surfaces  
22 of the substrate as described above and shown in Fig. 3. Even though  
23 such a process regime risks defective monolayer formation, such process

may be used to form a nucleation layer by ALD. The deposition layer may be formed in a traditional ALD process regime at lower temperature and pressure. For example, traditional ALD of silicon nitride may occur at a temperature of from about 400 °C to about 550 °C and a pressure of less than about 100 milliTor. Different ranges are also conceivable, as determinable by those skilled in the art, depending on deposition precursors, nucleation layer composition, surface properties, and other factors. Depending on the desired properties of the deposition layer, such layer may also be formed by ALD outside the traditional ALD process regime.

Another example of an *in situ* method involves chemical vapor deposition (CVD). The general technology of CVD includes a variety of more specific processes, including, but not limited to, plasma enhanced CVD and others. CVD is commonly used to form non-selectively a complete, deposited material on a substrate. One characteristic of CVD is the simultaneous presence of multiple species in the deposition chamber that react to form the deposited material. Such condition is contrasted with the purging criteria for traditional ALD wherein a substrate is contacted with a single deposition specie and chemisorbs to a substrate or previously deposited specie. A nontraditional ALD process regime may provide simultaneously contacted species of a type or under conditions such that ALD chemisorption, rather than CVD reaction occurs.

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1 As one example, U.S. Patent Application No. 09/619,449 filed July  
2 19, 2000 by Garo J. Derderian and Gurtej S. Sandhu entitled  
3 "Deposition Methods" and assigned to Micron Technologies, Inc. discloses  
4 a nontraditional ALD process and is herein incorporated by reference.  
5 Derderian et al. describe a deposition method including contacting a  
6 substrate with a first initiation precursor and forming a first portion of  
7 an initiation layer on the substrate. At least a part of the substrate is  
8 contacted with a second initiation precursor different from the first  
9 initiation precursor and a second portion of the initiation layer is formed  
10 on the substrate. The invention may include simultaneously contacting  
11 a substrate with a plurality of initiation precursors, forming on the  
12 substrate an initiation layer comprising components derived from each of  
13 the plurality of initiation precursors. However, the plurality of initiation  
14 precursors do not react together as in CVD. Rather, they chemisorb to  
15 the substrate, providing a surface onto which a deposition specie may  
16 next chemisorb to form a complete layer of desired material.

17 Under most CVD conditions, deposition of the material occurs  
18 largely independent of the composition or surface properties of an  
19 underlying substrate. However, deposition rate can be a frequent issue  
20 in performing CVD. High deposition rates are often desired to increase  
21 production output as long as such rates do not significantly diminish the  
22 quality of a deposited material. Accordingly, depending on the particular  
23 type of CVD technique, a process regime is selected that produces as

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1 high a deposition rate as is possible without significant negative impacts  
2 on material quality.

3 In the present aspect of the invention, deposition rate is a less  
4 significant issue. Accordingly, observation indicates that lower pressures,  
5 temperatures, plasma intensities, reactant concentrations, etc., than would  
6 otherwise be traditionally accepted may be used to produce a nucleation  
7 layer. CVD of a nucleation layer may thus occur at a deposition rate  
8 that conventionally might not qualify for a suitable CVD process. For  
9 example, traditional CVD of silicon nitride may occur at a temperature  
10 between about 600 °C to about 800 °C and a pressure between about  
11 100 milliTorr to about 2 Torr, depending on the selected temperature.  
12 If temperature is toward the low end of the range, then pressure is  
13 generally toward the high end of the range to stay within the traditional  
14 process regime. Exemplary parameters for nontraditional CVD of a  
15 nucleation layer may fall below one or both of such ranges or be in the  
16 low end of both ranges. Different ranges are conceivable, as  
17 determinable by those skilled in the art, depending on deposition  
18 precursors, substrate composition, surface properties, and other factors.

19 Since CVD is typically a non-selective form of deposition, the non-  
20 traditional process regime can produce a suitable nucleation layer having  
21 a thickness of one atom or molecule or more. Specifically, formation  
22 of an approximately 4 to 6 Angstrom silicon nitride nucleation layer from  
23 ammonia and dichlorosilane (DCS) has been achieved at a pressure of

less than approximately 1.5 Torr, a temperature of approximately 645°C, and a processing time of about 2 minutes. Depending on the CVD technique selected, the same reaction chamber or tool may be used both for CVD of a nucleation layer and ALD of a deposition layer. Thus, the hybrid structure of the CVD nucleation layer and ALD deposition layer may be formed possessing the advantageous qualities of an ALD material and such formation may be accomplished *in situ*.

Further, forming a deposition layer may occur by unconventional CVD in a process regime so far outside conventional CVD that the deposition is substantially selective. That is, multiple deposition species may contact the substrate together in the deposition chamber. However, temperature and pressure are low enough that the thickness of the deposition layer over a first part of a substrate is less than 50% of a thickness of the deposition layer over a second part, as shown in Fig. 2. Exemplary parameters include less than about 645 °C and less than about 500 Torr or perhaps different ranges, as determinable by those skilled in the art, depending on above mentioned factors. In such a process regime, pressure might bear a more significant effect on selectivity compared to temperature. The unconventional CVD process regime may be conducive to forming a deposition layer only about 1 to 5 atoms or molecules thick. Accordingly, by using a nucleation layer in keeping with the various aspects of the present invention, unconventional CVD may also be used to form a deposition layer.

As examples of *ex situ* processing, any of the above-described ALD or CVD techniques may be used. A substrate may be placed in a first chamber and the first and second parts of a nucleation layer formed on the substrate. The substrate may then be removed from the first chamber and placed in a second chamber different from the first. Formation of an ALD precursor monolayer or unconventional CVD layer may then occur in the second chamber. Accordingly, the first chamber may comprise any tool suitable for accomplishing CVD or ALD.

The first chamber may further comprise any tool suitable for accomplishing techniques such as rapid thermal nitridation (RTN), remote plasma nitridation (RPN), techniques for accomplishing growth of a material (as opposed to deposition) on a substrate, and other techniques. RTN, RPN, and other techniques can involve growth of a nucleation layer non-selectively on first and second surfaces of a substrate. RTN often occurs in an ammonia ambient at a temperature of greater than 700°C. Temperature may be limited to about 800°C in circumstances where thermal budget limitations exist. RPN is performed similarly except that a plasma is used to provide reactive nitrogen radicals in a manner that provides reduction of process temperature. Accordingly, RPN may be preferred in a circumstance with a sensitive thermal budget.

Material growth techniques, for example RTN, RPN, and others, may produce a nucleation layer the composition and selectivity of which can be influenced by the composition of the underlying substrate. For

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1 example, one potential substrate is one wherein first part 4 of substrate  
2 2 in Fig. 1 comprises BPSG and second part 6 comprises polysilicon.  
3 BPSG comprises silicon, oxygen, boron, and phosphorous. Polysilicon  
4 comprises primarily silicon. Both materials comprise silicon, accordingly,  
5 thermal growth techniques may produce a silicon-containing material  
6 grown on the substrate. Nitride growth techniques may produce silicon  
7 nitride on both materials. However, the silicon nitride material grown  
8 on BPSG may also include oxygen, for example, the material may  
9 comprise silicon oxynitride. Usually, the boron and phosphorous dopants  
10 of BPSG will not be incorporated into the grown material.

11 In some circumstances, one part of a substrate comprises silicon  
12 and another part of the substrate does not comprise silicon. Whether  
13 a nitride or other grown material will form on the substrate will depend  
14 on the susceptibility of the non-silicon-comprising material to such growth  
15 technique. Accordingly, a grown nucleation layer may form substantially  
16 non-selectively on a substrate or it may form selectively on a substrate  
17 depending on the criteria discussed above. Nevertheless, it is conceivable  
18 within the various aspects of the invention that an *ex situ* processing  
19 method may form a first and a second part of a nucleation layer  
20 simultaneously and substantially non-selectively on a first and second  
21 surface of a substrate. Such may occur even though the first surface of  
22 the substrate exhibits a property of chemisorbing a first precursor at a  
23 slower rate compared to the second surface. Deposition of a material

may subsequently occur on the *ex situ* formed nucleation layer also substantially non-selectively.

Another aspect of the invention holds specific application to forming container capacitor structures. Fig. 5 shows a semiconductive wafer construction 20 having partially formed dynamic random access memory (DRAM) cells formed thereon. Semiconductive wafer construction 20 includes a semiconductive material 22, for example, a bulk silicon wafer, and a field oxide 23 formed on semiconductive material 22. Node locations 25, 27, and 29 are formed within semiconductive material 22. Word lines 24 are formed over field oxide 23 and word lines 26 are formed over semiconductive material 22. An oxide layer 32 formed over word lines 24 and 26 prevents diffusion of dopants within a BPSG layer 34 into word lines 24 and 26. Capacitor openings 38 and 40 are formed through BPSG layer 34 to expose node locations 25 and 29, respectively. A storage node layer 36 is formed on BPSG layer 34 and in electrical connection with node locations 25 and 29. Storage node layer 36 may comprise polysilicon, or more preferably rugged polysilicon. Rugged polysilicon may include hemispherical grain polysilicon, spherical grain polysilicon, etc.

Formation of silicon nitride as a capacitor dielectric on storage node layer 36 is desired. Formation of silicon nitride on BPSG layer 34 as a dopant diffusion barrier is also desired. Formation of silicon nitride as a capacitor dielectric by ALD offers the advantage of a thin





1 nucleation layer within the low pressure CVD hot wall batch reactor.  
2 The deposition layer may be formed by ALD.

3 Alternatively, a silicon nitride nucleation layer may be formed *ex*  
4 *situ* using RTN at about 800 °C for about 60 seconds in an ammonia  
5 ambient. The substrate and nucleation layer may then be removed to  
6 a deposition device suitable for the deposition layer formation, such as  
7 by ALD.

8 In compliance with the statute, the invention has been described  
9 in language more or less specific as to structural and methodical  
10 features. It is to be understood, however, that the invention is not  
11 limited to the specific features shown and described, since the means  
12 herein disclosed comprise preferred forms of putting the invention into  
13 effect. The invention is, therefore, claimed in any of its forms or  
14 modifications within the proper scope of the appended claims  
15 appropriately interpreted in accordance with the doctrine of equivalents.  
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